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Dissolved CO_2 and alkane gas in clay formations

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Abstract

Characterization of dissolved CO_2 and alkane gas in clayrocks may help assessing the confinement properties of geological barriers considered as potential host rocks for a deep geological disposal as well as for caprocks of gas storages. A monitoring of alkanes with CO_2, combined with carbon isotopes was performed on core samples coming from Underground Research Laboratories (Bure, Mont Terri, Tournemire) and the Schlattingen borehole in France and Switzerland. Composition of hydrocarbon gas and $\delta^{13}C$ of methane strongly suggest a dominant thermogenic origin of methane which is mixed with a bacterial origin for the Toarcian shales, Pliensbachien and Callovian-Oxfordian clayrocks. Results also evidence the contrasted behavior of CO_2, which is controlled by chemical equilibrium between pore water and carbonate mineralogy, compared to the alkanes which are present in the porosity as a stock of dissolved gases which can be depleted during degassing experiments.

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1. Introduction

In several countries, deep nuclear waste repositories will be built in marine clay formations. Research studies on their pore water chemistry and reactive transport modelling have demonstrated the necessity to obtain some gas parameters (partial pressure of dissolved gas, gas diffusion rate…) to constrain the models[1, 2]. On the other hand, the host clay formations, which are initially under reduced conditions, will undergo various types of perturbations during the history of the disposal. The construction of access galleries and tunnels is assumed to induce first an oxidizing perturbation, while the closure of the repository should instead produce hydrogen by anoxic corrosion of carbon steel present in emplacement cells [3]. Moreover, the natural presence of carbonates in clayrock imposes a significant CO_2 partial pressure (P_{CO2}) inducing carbonation of cement materials at contact with clay[4]. Forecasting the impacts of

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such perturbations due to engineered materials needs to define the natural background of gas in the undisturbed clay formation. In that way, experiments have been conducted in different underground research laboratories (URL) and boreholes from Europe and have provided evidence of natural CO_2, N_2, alkanes and noble gases (He, Ar) dissolved in clayrock pore waters[1,3,5]. However the low permeability of such compacted clayrocks makes difficult to measure in situ the partial pressures of gas due to degassing of solutions[6]. Gas extraction by equilibration of fresh core samples in specific gas cells has been alternatively developed to analyze dissolved gas naturally released from cores at laboratory conditions[6,7,8,9]. A series of analyses has been realized first on core clay samples from different URLs with the goal of measuring the P_{CO2}, a required parameter to constrain pH of pore water and the pore water chemistry model. This work provides additional data of alkanes extracted with CO_2 for discussing their content and origins.

2. Core samples and analytical technique

All the core clay samples were collected in boreholes crosscutting Jurassic clay formations from/close to the Underground research Laboratory of Bure[7,8,9] (Pliensbachian and Callovian-Oxfordian clayrocks: Eastern Paris Basin, France), from the Tournemire Channel[10] (Upper and Lower Toarcian shales: South-eastern France), from the Mont Terri Channel[3] (Aalenian Opalinus clayrocks: Folded Jura, North-western Switzerland) and from the Schlattingen borehole[5] (Aalenian Opalinus clayrocks: Swiss Molasse Basin, North-eastern Switzerland). The Jurassic formations from the four sites have undergone different burial and tectonic evolutions.

Core samples (10 to 20 cm-long) were conditioned on the field immediately after the drilling. They were cleaned and cut on their rims, to eliminate the core surface contaminated by the drilling fluid, and weighted. Then they were conditioned in gas cells under a He pressure of about 600 mbars, after three short cycles of pumping alternating with He pressure. The amounts of CO_2, alkanes, O_2 and N_2 are regularly analyzed on a Varian Star 3400 CX gas chromatograph. O_2 and N_2 were regularly measured to verify the tightness of the gas cell. After stabilization of the P_{CO2}, a fraction of gas is recovered from the degassing cell by expansion into a vacuum line. Carbon isotope ratios of CO_2 were measured using a gas chromatography-based GasBench II system coupled to a Delta plus XP isotope ratio mass spectrometer (Thermo Finnigan). Compound-specific isotope analysis of gaseous hydrocarbons (CH_4 to C_4H_{10}) was performed using a Trace GC ultra gas chromatograph interfaced to a Delta plus XP isotope ratio mass spectrometer via a combustion furnace (Thermo Finnigan). In both cases, isotope ratios are determined relative to a CO_2 reference gas ($\delta^{13}C_{PDB}$ = -40.9 ± 0.3‰). For analytical details, please refer to Blessing et al. (AIG-11, 2015).

3. Results

The gas monitoring was performed till stabilization of the gas composition. Equilibration time takes several months; this time varies with the clay formation, the gas nature, but also with relative humidity[11]. CO_2 equilibration takes at least three months (Fig. 1a). Alkane monitoring of HT1 core samples from the Mont Terri channel provides evidence of an equilibration more rapid for CH_4 than C_2H_6, C_3H_8 and C_4H_{10} gases, which could be due to the molecule size (Fig. 1b).

Maximum values of P_{CO2} widely range between 1.7 and 20.4 mbar with most of the values around 5 mb (Tab. 1). The P_{CO2} values obtained on the eight core clay samples from the Schlattingen Borehole are almost homogeneous, although samples were collected at different depths and in different clay formations. On contrary the CO_2 gas equilibration of four core Opalinus Clay samples from the HT1 borehole at Mont Terri, which are very close to each other, provides evidence of high variation of the P_{CO2} (between 3.6 and 8.9 mb). The range of P_{CO2} measured at Schlattingen and values of 4-5 mb at Mont Terri are similar to values acquired previously at the Mont Terri rock lab [1, 6]. The high P_{CO2} variations observed for the HT1 core samples are attributed to the relative humidity measured in the gas cell and the saturation state of the core sample (Fig. 1); these results are in agreement with experimental data and modelling[11]. P_{CO2} data and the range of $\delta^{13}C_{CO2}$ (-15 to -10 ‰ PDB) confirm that CO_2 results from equilibrium between aqueous solution species and diagenetic carbonate minerals[9,11].

The alkane partial pressures ($P_{Alkanes}$) are generally low, except for Toarcian core samples. The highest values are measured in Lower Toarcian shales which contain about 6-10 vol % of organic matter which is mature and kerogenic [12]. High $P_{Alkanes}$ values are also measured in Upper Toarcian shales eventhough their organic matter content is much lower (about 1% vol), and similar to that of the other studied clay formations (Aalenian, Callovian-

Oxfordian, Pliensbachian). The C1/(C2 + C3) ratio is generally low (0.5-6.1). It is noteworthy that 1) for the same clay formation, $P_{Alkanes}$ are not correlated with P_{CO2}, and 2) in reconditioned gas cells of core clay samples of Aalenian, Callovian-Oxfordian and Upper Toarcian age, $P_{Alkanes}$ are significantly lower than those measured in the first stage of conditioning, while P_{CO2} remains unchanged. These results strongly suggest different mechanisms for the control of dissolved CO_2 and alkanes. CO_2 results from equilibrium between aqueous solution species and diagenetic carbonate minerals, whereas alkane partial pressures are probably controlled by an initial stock of dissolved gas (only gas diffusion through the rock). CH_4 presents significant isotopic variations from one formation to another (from -66 to -33 ‰ PDB), whereas $\delta^{13}C$ of other alkanes are relatively homogeneous (-43 to -31 ‰ PDB). Elevated $\delta^{13}C_{CH4}$ values (-47 to -33 ‰ PDB) combined with low C1/(C2+C3) ratios indicate that hydrocarbon gases are essentially of thermogenic origin in the Opalinus core samples at Schlattingen and at the Mont Terri URL, and in the Pliensbachian core sample from Bure. Elsewhere lower $\delta^{13}C_{CH4}$ values (-66 to -63 ‰ PDB) combined with low C1/(C2+C3) ratios suggest that hydrocarbon gases are a mixture of thermogenic methane (-50 to -30 ‰ PDB) and of bacterial methane (-90 to -70 ‰ PDB)[13].

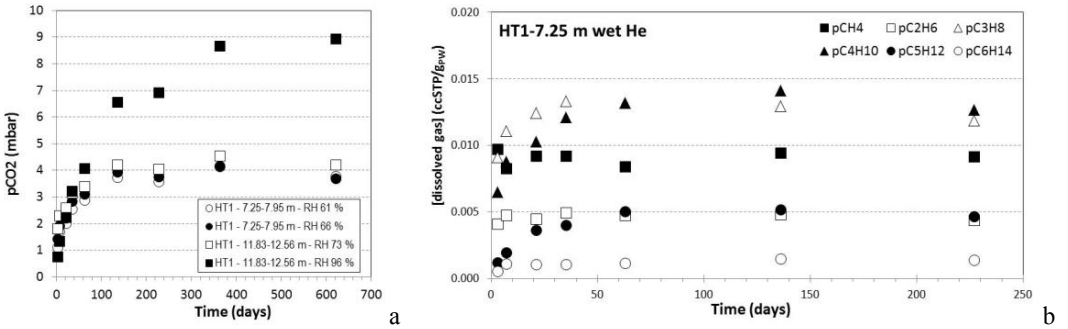

Fig. 1. Monitoring of gas partial pressures in HT core samples at Mont Terri (a) $CO_{2(g)}$; (b) concentrations of alkanes (given in ccSTP/g of pore water) in HT1-7.25 m core sample.

Table 1. Range of CO_2 and alkane partial pressures (in mbar) and corresponding $\delta^{13}C$ (‰ PDB) obtained at the four sites.

	Tournemire (SE, France)		Schlattingen (NE, Switzerland)	Mont Terri (NW, Switzerland)	Bure (NE, France)	
	Lower Toarcian	Upper Toarcian	Aalenian	Aalenian	Pliensbachian	Callovian-Oxfordian *
T max (°C)	80-120		85	85	45	45
TOC (wt %)	6-10	~1-2	~1	~1	~1	~1
P_{CO2}	6.4-20.4	3.6-14.6	4.2-6.1	3.6-8.9	7.0	1.7-11.6
$\delta^{13}C_{CO2}$	-10	-10	-12	-11.5	-15	-10/-6
P_{CH4}	112-146	24-29	0.3-3.2	0.6-0.8	1.3	
$\delta^{13}C_{CH4}$	-66	-63/-61	-37/-33	-37	-47	-62/-49
P_{C2H6}	16.2-19.7	4.3-4.4	0.1-0.6	0.3-0.4	0.2	
$\delta^{13}C_{C2H6}$	-41	-41	-37/-36	-43	-35	-43/-25
P_{C3H8}	20.2-25.3	6.2-6.3	0.1-0.7	0.8-0.9	0.15	
$\delta^{13}C_{C3H8}$	-35	-35	-36/-35	-36	-34	-38/-30
P_{C4H10}	11.8-14.6	3.5-3.6	0.1-0.6	0.8-0.9	-	
$\delta^{13}C_{C4H10}$	-32	-32	-33/-31	-33		
C1/C2+C3	5.9-6.1	4.2-4.6	2.8-4.6	0.5-0.6	4.0	1.7-3.1

4. Conclusion

Characterization of gases dissolved in pore water of clayrocks is required to understand the containment properties of clayrocks studied for hosting a deep geological disposal or acting as a caprock. In this context, the

method developed initially for measuring P_{CO2} in the clayrock pore water, was also used to extract alkanes. A systematic monitoring of alkanes with CO_2, combined with carbon isotopes was performed on core samples coming from various underground laboratories (Bure, Mont Terri, Tournemire) and exploration borehole (Schlattingen) in France and Switzerland. Alkanes are generally wet, i.e. rich in C2+ compounds. It is proposed that CO_2 possibly results from equilibrium between aqueous solution species and diagenetic carbonate minerals. On the contrary, C1/(C2+C3) ratios and $\delta^{13}C_{CH4}$ strongly suggest a dominant thermogenic origin of alkanes, mixed with a bacterial origin for Toarcian shales, such as Callovian-Oxfordian clayrocks[13]. Thermogenic gases are formed by organic matter maturation under thermal stress (> 80 °C). Characterization of organic matter in Upper Toarcian and Callovian-Oxfordian clay formations demonstrated that none of them is mature [14,15], and consequently cannot be considered as the source of thermogenic gases (diffusive gas). In Opalinus clay from the Mont Terri and Schlattingen, organic matter is at the limit of the oil window and could be potentially for a small part the source of thermogenic gas[16]. Lower Toarcian black shales at Tournemire are clearly different from other Jurassic clay formations by their high organic matter content and their high dissolved methane gas, and could be considered as the source of thermogenic gas in the upper Toarcian.

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